Multi-channel curve crossing problems: Analytically solvable model

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We have proposed a general method for finding the exact analytical solution for the multi-channel curve crossing problem in presence of delta function couplings. We have analyzed the case where a potential energy curve couples to a continuum (in energy) of potential energy curves.

I. INTRODUCTION:

Nonadiabatic transition due to potential curve crossing is one of the most important mechanisms to effectively induce electronic transitions [1]. This is a very interdisciplinary concept and appears in almost all fields of physics and chemistry, even in biology [2]. The common examples are variety of atomic and molecular processes such as atomic and molecular collisions, chemical reactions and molecular spectroscopic processes. Attempts have been made to classify organic reactions by curve crossing diagrams [3]. There are also examples in nuclear physics [4, 5]. Two state curve crossing can be classified into the following two cases according to the crossing scheme: (1) Landau-Zener (L.Z) case, in which the two diabatic potential curves has the same signs for the slopes and (2) non-adiabatic tunnelling (N.T) case, in which the diabatic curves has the opposite sign of slopes. In our earlier paper [6] paper we have considered two diabatic curves, crossing each other and there is a coupling between the two curves, which causes transitions from one curve to another. This transition would occur in the vicinity of the crossing point. In particular, it will occur in a narrow range of x, given by

$$V_1(x) - V_2(x) \simeq V_{12}(x_c) \tag{1}$$

where x denotes the nuclear coordinate and x_c is the crossing point. V_1 and V_2 are determined by the shape of the diabatic curves and V_{12} represent the coupling between them. Therefore it is interesting to analyse a model, where coupling is localized in space near x_c. Thus we

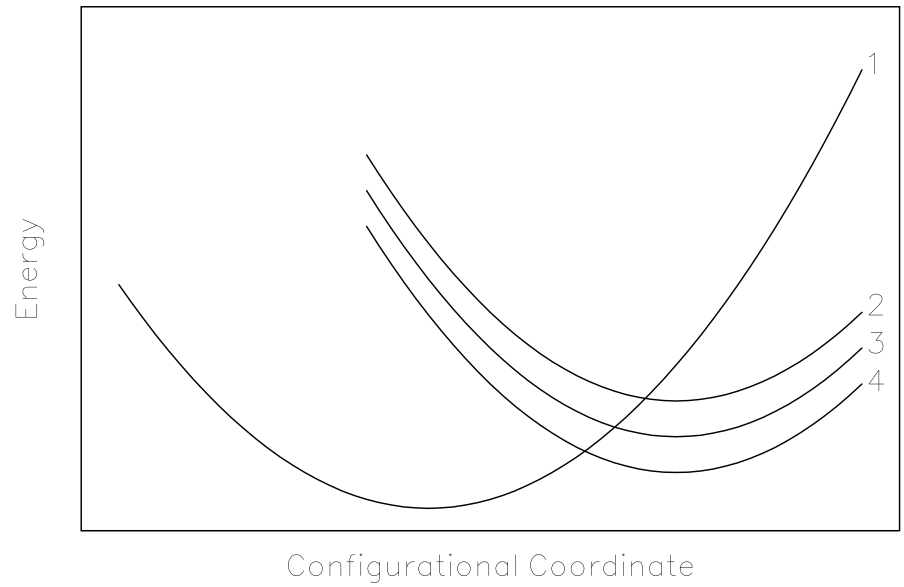

FIG. 1: The multi-channel curve crossing problem.

put

$$V_{12}(x) = K_0\delta(x - x_c) \tag{2}$$

here K_0 is a constant. This model has the advantage that it can be exactly solved [6]. In this paper we apply this model in the case of general multi-channel problems (Fig. 1), since this is very important in view of the applications to various practical problems in chemical dynamics beyond simple diatomic systems. Using model potential in which one linear diabatic potential intersects many constant diabatic potentials, Demkov and Osherov [7] showed that the state to state transition probabilities can be exactly calculated by a product of the Landau-Zener probabilities at each crossing. A more general model, in which one set of parallel linear diabatic potentials intersect with another set of parallel ones, has been analyzed by Child [8]. Korsch [9] reported multi-state curve crossing problems by the Magnus approximation, and later Nakamura [1] analyzed the problems by complex phase-integral technique. In the following we give a general procedure for finding the exact quantum mechanical solution for multi-channel curve crossing problem by extending our two state model [6].

II. TWO STATE PROBLEM

The time dependent Schrö dinger equation (we take $\hbar = 1$ here and in subsequent calculations)

$$i\frac{\partial\Psi(x,t)}{\partial t} = H\Psi(x,t). \tag{3}$$

H is defined by

$$H = \begin{pmatrix} H_1(x) & V(x) \\ V(x) & H_2(x) \end{pmatrix}, \tag{4}$$

where $H_i(x)$ is

$$H_i(x) = -\frac{1}{2m}\frac{\partial^2}{\partial x^2} + V_i(x). \tag{5}$$

and

$$\Psi(x,t) = \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \end{pmatrix}, \tag{6}$$

$\psi_1(x,t)$ and $\psi_2(x,t)$ are the probability amplitude for the two states. We find it convenient to define the half Fourier Transform $\overline{\Psi}(\omega)$ of $\Psi(t)$ by

$$\overline{\Psi}(\omega) = \int_0^\infty \Psi(t)e^{i\omega t}dt. \tag{7}$$

Half Fourier transformation of Eq. (3) leads to

$$\begin{pmatrix} \overline{\psi}_1(\omega) \\ \overline{\psi}_2(\omega) \end{pmatrix} = i\begin{pmatrix} \omega - H_1 & V \\ V & \omega - H_2 \end{pmatrix}^{-1}\begin{pmatrix} \psi_1(0) \\ \psi_2(0) \end{pmatrix}. \tag{8}$$

This may be written as

$$\overline{\Psi}(\omega) = iG(\omega)\Psi(0). \tag{9}$$

$G(\omega)$ is defined by $(\omega - H)\ G(\omega) = I$. In the position representation, the above equation may be written as

$$\overline{\Psi}(x,\omega) = i\int_{-\infty}^{\infty} G(x,x_0;\omega)\overline{\Psi}(x_0,\omega)dx_0, \tag{10}$$

where $G(x,x_0;\omega)$ is

$$G(x,x_0;\omega) = \langle x|(\omega - H)^{-1}|x_0\rangle. \tag{11}$$

Writing

$$G(x,x_0;\omega) = \begin{pmatrix} G_{11}(x,x_0;\omega) & G_{12}(x,x_0;\omega) \\ G_{21}(x,x_0;\omega) & G_{22}(x,x_0;\omega) \end{pmatrix} \tag{12}$$

and we can write

$$G_{11}(x, x_0; \omega) = \langle x|[\omega - H_1 - V(\omega - H_2)^{-1}V]^{-1}|x_0\rangle. \tag{13}$$

This expression simplify considerably if V is a delta function located at x_c. In that case V may be written as $V = K_0 S = K_0\ |x_c\rangle\ \langle x_c|$. Then

$$G_{11}(x, x_0; \omega) = \langle x|[\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega)S]^{-1}|x_0\rangle, \tag{14}$$

where

$$G_2^0(x, x_0; \omega) = \langle x|(\omega - H_2)^{-1}|x_0\rangle, \tag{15}$$

Now we use the operator identity

$$(\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega)S)^{-1} = (\omega - H_1)^{-1} + (\omega - H_1)^{-1} K_0^2 G_2^0(x_c, x_c; \omega)S[\omega - H_1 - K_0^2 G_2^0(x_c, x_c; \omega)S]^{-1}.$$

Inserting the resolution of identity $I = \int_{-\infty}^{\infty} dy\ |y\rangle\ \langle y|$ in the second term of the above equation, we arrive at

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + K_0^2 G_1^0(x, x_c; \omega) \times G_2^0(x_c, x_c; \omega) G_{11}(x_c, x_0; \omega). \tag{16}$$

Putting $x = x_c$ in Eq. (16) and solving for $G_{11}(x_c, x_0; \omega)$ gives

$$G_{11}(x_c, x_0; \omega) = G_1^0(x_c, x_0; \omega) \times [1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)]^{-1}. \tag{17}$$

This when substituted back into Eq. (16) gives

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + \frac{K_0^2 G_1^0(x, x_c; \omega) G_2^0(x_c, x_c; \omega) G_1^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}. \tag{18}$$

Using the same procedure one can get

$$G_{12}(x, x_0; \omega) = \frac{K_0 G_1^0(x, x_c; \omega) G_2^0(x_c, x_0; \omega)}{1 - K_0^2 G_1^0(x_c, x_c; \omega) G_2^0(x_c, x_c; \omega)}. \tag{19}$$

Similarly one can derive expressions for $G_{22}(x, x_0; \omega)$ and $G_{21}(x, x_0; \omega)$.

III. FORMULATION OF MULTI-CHANNEL CURVE CROSSING THEORY

We start with the time dependent Schrödinger equation for a three state system (we put $\hbar = 1$)

$$i\frac{\partial}{\partial t}\begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \\ \psi_3(x,t) \end{pmatrix} = \begin{pmatrix} H_{11}(x) & V_{12}(x) & V_{13}(x) \\ V_{21}(x) & H_{22}(x) & 0 \\ V_{31}(x) & 0 & H_{33}(x) \end{pmatrix} \begin{pmatrix} \psi_1(x,t) \\ \psi_2(x,t) \\ \psi_3(x,t) \end{pmatrix} \tag{20}$$

The above equation can be splitted into

$$i\frac{\partial\psi_1(x,t)}{\partial t} = H_{11}(x)\psi_1(x,t) + V_{12}(x)\psi_2(x,t) + V_{13}(x)\psi_3(x,t) \tag{21}$$

and

$$i\frac{\partial\psi_2(x,t)}{\partial t} = V_{21}(x)\psi_1(x,t) + H_{22}(x)\psi_2(x,t) \tag{22}$$

and also

$$i\frac{\partial\psi_3(x,t)}{\partial t} = V_{31}(x)\psi_1(x,t) + H_{33}(x)\psi_3(x,t) \tag{23}$$

We define half Fourier transform $\overline{\Psi}(\omega) = \int_0^\infty \Psi(t)e^{i\omega t}dt$ and Fourier transform of the above three equations gives

$$-i\psi_1(x,0) + \omega\overline{\psi}_1(x,\omega) = H_{11}(x)\overline{\psi}_1(x,\omega) + V_{12}(x)\overline{\psi}_2(x,\omega) + V_{13}(x)\overline{\psi}_3(x,\omega) \tag{24}$$

and

$$\omega\overline{\psi}_2(x,\omega) = V_{21}(x)\overline{\psi}_1(x,\omega) + H_{22}(x)\overline{\psi}_2(x,\omega) \tag{25}$$

as $\psi_2(x,0) = 0$. Also

$$\omega\overline{\psi}_3(x,\omega) = V_{31}(x)\overline{\psi}_1(x,\omega) + H_{33}(x)\overline{\psi}_3(x,\omega) \tag{26}$$

As $\psi_2(x,0) = 0$. We will substitute $\overline{\psi}_2(x,\omega)$ and $\overline{\psi}_3(x,\omega)$ in Eq. (24)

$$\overline{\psi}_2(x,\omega) = [\omega - H_{22}(x)]^{-1}V_{21}(x)\psi_1(x) \tag{27}$$

and

$$\overline{\psi}_3(x,\omega) = [\omega - H_{33}(x)]^{-1}V_{31}(x)\psi_1(x) \tag{28}$$

Eq. (24) becomes

$$[\omega - H_{11}(x) - V_{12}(x)[\omega - H_{22}(x)]^{-1}V_{21}(x) - V_{13}(x)[\omega - H_{33}(x)]^{-1}V_{31}(x)]\overline{\psi}_1(x,\omega) = i\psi_1(x,0) \tag{29}$$

The above equation simplify considerably if the couplings are assumed to be Dirac Delta function, which in operator notation may be written as $V_{21} = V_{12} = K_2 S = K_2 |x_{12}\rangle\langle x_{12}|$ and $V_{31} = V_{13} = K_3 S = K_3 |x_{13}\rangle\langle x_{13}|$. The above equation may be written as

$$[(\omega - H_{11}(x)) - K_2^2 \delta(x - x_{12}) G_2^0(x_{12}, x_{12}; \omega) - K_3^2 \delta(x - x_{13}) G_3^0(x_{13}, x_{13}; \omega)] \overline{\psi}_1(x, \omega) = i\psi_1(x, 0) \tag{30}$$

or

$$[(\omega - H_{12}(x)) - K_3^2 \delta(x - x_{13}) G_3^0(x_{13}, x_{13}; \omega)] \overline{\psi}_1(x, \omega) = i\psi_1(x, 0) \tag{31}$$

where,

$$H_{12}(x) = H_{11} + K_2^2 \delta(x - x_{12}) G_1^0(x_{12}, x_{12}; \omega) \tag{32}$$

The solution of this equation may be expressed in terms of the Green's function $G'(x, x_0; \omega)$

$$[(\omega - H_{12}(x)) - K_3^2 \delta(x - x_{13}) G_3^0(x_{13}, x_{13}; \omega)] G'(x, x_0; \omega) = i\delta(x - x_0) \tag{33}$$

Also

$$\overline{\psi}_1(x, \omega) = i \int_{-\infty}^{\infty} dx_0 G'(x, x_0; \omega) \psi_1(x, 0) \tag{34}$$

Here $G'(x, x_0; \omega)$ is

$$G'(x, x_0; \omega) = \langle x | (\omega - H_{13})^{-1} | x_0 \rangle \tag{35}$$

where

$$H_{13} = H_{12}(x) + K_3^2 \delta(x - x_{13}) G_3^0(x_{13}, x_{13}; \omega) \tag{36}$$

In the previous section we have calculated $G_{11}(x, x_0; \omega)$, which is redefined below

$$G_{11}(x, x_0; \omega) = \langle x | (\omega - H_{12})^{-1} | x_0 \rangle \tag{37}$$

The $G_{11}(x, x_0; \omega)$ can be written

$$G_{11}(x, x_0; \omega) = G_1^0(x, x_0; \omega) + \frac{K_2^2 G_1^0(x, x_{12}; \omega) G_2^0(x_{12}, x_{12}; \omega) G_1^0(x_{12}, x_0; \omega)}{1 - K_2^2 G_1^0(x_{12}, x_{12}; \omega) G_2^0(x_{12}, x_{12}; \omega)} \tag{38}$$

In this case, one can find the Green's function $G_{11}(x, x_0; \omega)$, using the method as we have used before.

$$G'(x, x_0; \omega) = G_{11}(x, x_0; \omega) + \frac{K_3^2 G_{11}(x, x_{13}; \omega) G_3^0(x_{13}, x_{13}; \omega) G_{11}(x_{13}, x_0; \omega)}{1 - K_3^2 G_{11}(x_{13}, x_{13}; \omega) G_3^0(x_{13}, x_{13}; \omega)} \tag{39}$$

So in this way one can add the effect of 4-th state, 5-th state etc. one by one and calculate Green's function for N-channel problem.

A. Multi-channel curve crossing problem: an analytically solvable continuum model

Here we start with N-channel generalization of Eq. (24, 25, 26)

$$-i\psi_1(x,0)+\omega\overline{\psi}_1(x,\omega)=H_{11}(x)\overline{\psi}_1(x,\omega)+\sum_{\varepsilon=2}^{N}V_{1\varepsilon}(x)\overline{\psi}_\varepsilon(x,\omega) \tag{40}$$

and

$$\omega\overline{\psi}_\varepsilon(x,\omega)=V_{\varepsilon 1}(x)\overline{\psi}_1(x,\omega)+H_{\varepsilon\varepsilon}(x)\overline{\psi}_\varepsilon(x,\omega) \tag{41}$$

From the Eq. (41) we calculate $\overline{\psi}_\varepsilon(x,\omega)$

$$\overline{\psi}_\varepsilon(x,\omega)=[\omega-H_{\varepsilon\varepsilon}(x)]^{-1}V_{\varepsilon 1}(x)\overline{\psi}_1(x,\omega) \tag{42}$$

So Eq. (40) can be written as

$$-i\psi_1(x,0)+\omega\overline{\psi}_1(x,\omega)=H_{11}(x)\overline{\psi}_1(x,\omega)+\sum_{\varepsilon=2}^{N}V_{1\varepsilon}(x)[\omega-H_{\varepsilon\varepsilon}(x)]^{-1}V_{\varepsilon 1}(x)\overline{\psi}_1(x,\omega) \tag{43}$$

we take $V_{\varepsilon 1}(x)=V_{1\varepsilon}(x)=k_\varepsilon(x)\delta(x-x_\varepsilon)$. The above expression becomes

$$-i\psi_1(x,0)+\omega\overline{\psi}_1(x,\omega)=H_{11}(x)\overline{\psi}_1(x,\omega)+\sum_{\varepsilon=2}^{N}k_\varepsilon(x)^2\delta(x-x_\varepsilon)G^0_\varepsilon(x_\varepsilon,x_\varepsilon;\omega)\overline{\psi}_1(x,\omega) \tag{44}$$

where

$$\begin{aligned}G^0_\varepsilon(x_\varepsilon,x_\varepsilon;\omega)&=\langle x_\varepsilon|[\omega-H_{\varepsilon\varepsilon}(x)]^{-1}|x_\varepsilon\rangle\\&=\sum_{n=0}^{\infty}\langle x_\varepsilon|\phi_n\rangle[\omega-H_{\varepsilon\varepsilon}(x)]^{-1}\langle\phi_n|x_\varepsilon\rangle\\&=\sum_{n=0}^{\infty}\phi^\varepsilon_n(x_\varepsilon)[\omega-H_{\varepsilon\varepsilon}(x)]^{-1}\phi^{\varepsilon *}_n(x_\varepsilon)\end{aligned} \tag{45}$$

In the above expression, ε takes discrete values. Now

$$[(\omega-H_{11}(x))-\sum_{\varepsilon=2}^{N}k_\varepsilon(x)^2\delta(x-x_\varepsilon)G^0_\varepsilon(x_\varepsilon,x_\varepsilon;\omega)]\overline{\psi}_1(x,\omega)=i\psi_1(x,0) \tag{46}$$

The solution of this equation may be expressed in terms of the Green's function $G''(x,x_0;\omega)$

$$[(\omega-H_{11}(x))-\sum_{\varepsilon=2}^{N}k_\varepsilon(x)^2\delta(x-x_\varepsilon)G^0_\varepsilon(x_\varepsilon,x_\varepsilon;\omega)]G''(x,x_0;\omega)=i\delta(x-x_0) \tag{47}$$

Here $G''(x,x_0;\omega)$ is

$G''(x,x_0;\omega) = \langle x|[(\omega - H_{11}(x)) - \sum_{\varepsilon=2}^{N} k_\varepsilon(x)^2\delta(x-x_\varepsilon)G^0_\varepsilon(x_\varepsilon,x_\varepsilon;\omega)]^{-1}|x_0\rangle$. Also

$$\overline{\psi}_1(x,\omega) = i\int_{-\infty}^{\infty} dx_0 G''(x,x_0;\omega)\psi_1(x,0) \tag{48}$$

In the continuum limit (here ε changes continuously), the expression for $G''(x,x_0;\omega)$ can be written

$$G''(x,x_0;\omega) = \langle x|[(\omega - H_{11}(x)) - \int_0^\infty d\varepsilon k(x,\varepsilon)^2\delta[x-x(\varepsilon)]G^0\{x(\varepsilon),x(\varepsilon);\omega,\varepsilon\}]^{-1}|x_0\rangle \tag{49}$$

In a very special case where all states couples at one point to the first one i.e. $x(\varepsilon) = a$

$$G''(x,x_0;\omega) = \langle x|[(\omega - H_{11}(x)) - \delta(x-a)\int_0^\infty d\varepsilon k(x,\varepsilon)^2 G^0(a,a;\omega,\varepsilon)]^{-1}|x_0\rangle \tag{50}$$

The above expression is very general and applicable to any potential. We can write Eq. (50) in a simplified form

$$G''(x,x_0;\omega) = \langle x|[(\omega - H_{11}(x)) - \delta(x-a)V(x,\omega]^{-1}|x_0\rangle \tag{51}$$

where

$$V(x,\omega) = \int_0^\infty d\varepsilon k(x,\varepsilon)^2 G^0[a,a;\omega,\varepsilon] \tag{52}$$

Special case

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In the following, we discuss the case where one potential (general) is coupled to continuum (in energy) of constant potentials at a point. Green's function for uncoupled potential is given by

$$G^0(a,a;\omega,\varepsilon) = \frac{1}{\hbar}\sqrt{\frac{m}{2(\hbar\omega - \varepsilon)}} \tag{53}$$

In the above expression ε varies continuously from 0 to ∞.

Analytical form of $V(x,E)$ depends on the functional form of $k(x,\varepsilon)$. For our calculation we take

$$k(x,\varepsilon)^2 = a\hbar\sqrt{\frac{2(\hbar\omega-\varepsilon)}{m}}e^{-\frac{\varepsilon}{\hbar\omega}} \tag{54}$$

So

$$V(x,\omega) = a\int_0^\infty d\varepsilon e^{-\frac{\varepsilon}{\hbar\omega}} = a\hbar\omega \tag{55}$$

The Eq. (51) now becomes

$$G''(x,x_0;\omega) = \langle x|[(\omega - H_{11}(x)) - \delta(x-a)a\hbar\omega]^{-1}|x_0\rangle \tag{56}$$

The above expression can be evaluated exactly.

IV. CONCLUSIONS:

We have extended our two state model to deal with general one dimensional multi-channel curve crossing problems in presence of delta function couplings. We have analyzed the case where a potential energy curve couples to a continuum (in energy) of potential energy curves. Nonadiabatic tunneling in an ideal one dimensional semi-infinite periodic potential system is also analyzed using our model. The same procedure is also applicable to the case where S is a non-local operator, and may be represented by $S \equiv |f\rangle\ K_0\ \langle g|$, f and g are arbitrary acceptable functions. Choosing both of them to be Gaussian will be an improvement over the delta function coupling model. S can also be a linear combination of such operators.

V. ACKNOWLEDGMENTS:

The author thanks Prof. K. L. Sebastian for suggesting intersting problems.

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